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DRIED FRUIT POWDER OF NEEM (*Azadirachta Indica*) FOR REMOVAL OF LEAD IONS FROM AQUEOUS SOLUTION BY ADSORPTION

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ABSTRACT

In the present study, Dried fruit powder of neem (*Azadirachta indica)* was used for the removal of lead ions from an aqueous solution by adsorption. The batch experiments were conducted for biosorption of Pb (II) on biosorbent by altering the various parameters, including pH—dose of biosorbents, concentration of metal ions solution, and contact time. The surface area, functionality, surface morphology, and elemental analysis of biosorbent were analyzed by Brunauer-Emmett-Teller, Fourier Transform Infrared Spectroscopy, and Field emission scanning electron microscopy with Energy-dispersive X-ray respectively. The adsorption isotherm models and kinetics study were done. The Neem (*Azadirachta indica*) fruit biosorbent exhibited the ability to remove 70% of Pb (II) from the aqueous solution with 20 mg/L of lead at a biosorbent dose of 2g/L. the study observed that removal efficiency increased as contact time increased, reaching saturation in approximately 90 minutes at optimum pH ~ 5. The best-fit models for the biosorption of heavy metal ions were pseudo-second-order kinetics and Langmuir adsorption isotherm, with a maximum adsorption capacity of 14.71 mg/g. The thermodynamic analysis indicated that the adsorption of these heavy metal ions was a spontaneous and endothermic process. The research indicates that neem (*Azadirachta indica*) fruit has the potential to be extensively studied as a highly effective biosorbent for removing metal ions from aqueous solution.

Keywords: *Azadirachta Indica*, Heavy Metal Ions, Biosorption, Batch Studies, Adsorption Capacity, Kinetic Study Langmuir

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INTRODUCTION

The continuing discharge of both organic and inorganic pollutants, such as synthetic chemicals and hazardous heavy metals from industrial wastewater, has emerged as a challenging problem in recent years. Due to the persistency and non-biodegradability nature of the heavy metals, these are toxic for human beings.[1] The issue of water pollution caused by heavy metal ions has attracted considerable interest because of its adverse impact on the environment and associated health risks. Lead is a highly enduring toxic heavy metal that can be commonly found in the environment. Lead can be present in industrial waste and occasionally in drinking water. Industrial origins of lead in water consist of acid battery, glass production, tanning, ceramic, and printing.[2] The contamination of drinking water has been attributed to the leaching of lead pipes into tap water. Exposure to organic pollutants and heavy metal compounds can lead to chronic and hazardous acute toxicities in aquatic organisms, plants, and humans. Exposure to lead adversely affects human health and lead accumulation in the human body leads to disruptions in immune system function.[3] According to the US Environmental Protection Agency (EPA), the acceptable limit for lead in drinking water is 0.05 mg/l. Consequently, even a low concentration of lead in water can be extremely hazardous.[4] Various traditional techniques have been suggested for the purification of wastewater. These techniques encompass chemical precipitation, ion exchange, filtration membrane, coagulation, electrochemical reduction, and reverse osmosis, and biological processes.[5] The significant drawback associated with these methods is their exorbitant expenses. In recent times, scientists have dedicated significant endeavors to discover alternative methods that are both cost-effective and efficient. In this regard, adsorption has proven to be more advantageous than alternative methods for water treatment in terms of cost, ease of operation, and flexibility of design, and does not produce by-products of harmful substances commonly associated with most processes.[6] Biosorption is an excellent method for eliminating heavy metals from the aqueous solution due to the ready availability of biosorbents, cost-effectiveness, and remarkable natural affinity

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towards metal ions. This process is rapid and based on the physio-chemical interactions between the metal ions and the functional groups present on the surface of the biosorbent. Numerous studies have documented the successful removal of lead from the aqueous solution using various biomass materials such as *Prunus dulcis* seed shell[7], pumpkin peel[8], Broadleaf Cattail and Water Hyacinth[9], *Ageratum conyzoid* biomass[10], etc. In this study, our objective is to utilize fallen fruits of neem (*Azadirachta indica*) from the neem plant, commonly found in local areas, as a biosorbent for removing lead from the aqueous solutions. We will analyze the various parameters that impact the biosorption process, as well as evaluate the equilibrium, kinetics, and mechanism models that govern this process.

EXPERIMENTAL

Plant Material

Plant material i.e. fruits of neem (*Azadirachta indica*) was collected from the Botanical garden of Chaudhary Charan Singh Haryana Agricultural University (Hisar), Haryana. The neem Fruits (Fig.-1) were collected from the Botanical Garden, CCSHAU (Hisar), Haryana. Fruits with inert material were washed with ordinary water and then with distilled water to get rid of dirt. The cleaned neem fruits were placed in an open environment for three days to allow moisture on their surface to evaporate, followed by drying in an oven at the temperature of 115ºC for a duration of 24 hours. The dried fruits were ground into powder with the electrical grinder and sieved through an 80 BSS stainless steel sieve. The powder was kept in an air-tight bottle for use in the experiments with the required amounts.

Fig.-1: Neem (*Azadirachta indica*) Fruits

Chemicals

Metal salts such as lead nitrate [Pb $(NO_3)_2$], were purchased from the Himedia Laboratories Private Limited. Hydrochloric acid and sodium hydroxide pellets were purchased from Central Drug House (P) Ltd. And used for the pH adjustment during the experiments.

Batch Biosorption Experiments

The batch experiments were conducted for biosorption of Pb (II) on neem fruit biosorbent. In the present research, the removal efficiency of fruit biosorbent was evaluated by altering various parameters. In order to determine the optimal *p*H level, 20 mL solutions with an initial concentration of 20 ppm of metal ions solution, and a constant dose of biosorbent (0.02g) were prepared at a range of pH values (2, 3, 4, 5, 6, 7, 8, and 9) at a contact time of 60 min. At the optimized pH, various quantities of biosorbents, specifically 0.01 g, 0.02 g, 0.04 g, 0.06 g, 0.08 g, 0.1 g, and 0.2 g, were utilized for the purpose of optimizing the dose of biosorbent. In addition, at optimized pH and biosorbent dose, metal solutions were formulated at various concentrations of 20, 30, 40, 50, 60, 70, and 80 ppm to further optimize the initial concentration. Lastly, to optimize the contact time, experiment allows at different intervals of time (30, 60, 90, 120, 150, 180, and 210 min.). The mixtures were subsequently stirred in a rotary shaker operating at 200 rpm and temperature of 303K. Upon the completion of each adsorption experiment, samples were separated into solid and liquid components through centrifugation at a speed of 4000-5000 rpm for a duration of 10-15 minutes. The flame atomic absorption spectroscopy (FAAS) method, utilizing Thermo Scientific equipment, was employed to determine the concentration of lead (Pb^{2+}) metal ions in the solution, expressed in mg/L. In this technique, acetylene gas served as the fuel to generate a flame with a high temperature of approximately 2500 K. The maximum absorbance was measured at a wavelength specifically set for the detection of Pb^{2+} ions, which occurred at 216.9 nm.

Calculations

The amount of Pb^{2+} metal ions that are adsorbed per gram of biosorbent at equilibrium can be calculated using equation 1.

$$q_e = \frac{(C_i - C_f)V}{m} \quad (1)$$

where, q_e denotes the maximum adsorption capacity (mg/g) at the equilibrium of the biosorbent, while C_f (mg/L) indicates the initial concentration of metal ions, and C_f denotes the final concentration of metal ions at the equilibrium time t in mg/L, and V represents the volume of the solution measured in liters, while m indicates the mass of the biosorbents expressed in grams. The experimental data concerning the biosorption of Pb (II) metal ions, was analyzed using the Langmuir[11] and Freundlich[12] adsorption isotherm models. The linear and nonlinear representations of the Langmuir isotherm are provided by equations 2 and 3.

$$\frac{C_e}{q_e} = \frac{1}{K_L \times q_{max}} + \frac{C_e}{q_{max}} \quad (2)$$

$$q_e = \frac{K_L \times q_{max} \times C_e}{1 + K_L \times C_e} \quad (3)$$

Linear and nonlinear forms of Freundlich adsorption isotherm are represented in equations (4) and (5) given below:

$$log\ q_e = logK_f + \frac{1}{n} logC_e \quad (4)$$

$$q_e = K_f \times (C_e)^{1/n} \quad (5)$$

where is the Langmuir constant, K_L depicts the stronger affinity of the metal ions with the biosorbent. The Freundlich isotherm parameters 1/n and K_f expressed as the heterogeneity factor, indicate the adsorption intensity and are related to the adsorption capacity of the material, respectively. The adsorption process was examined through the kinetics pseudo-first order[13] and pseudo-second order[14] models. The equations that represent these models are provided as equation (6) and (7), respectively:

$$q_t = q_e(1 - e^{-K_1 t}) \quad (6)$$

$$q_t = \frac{(q_e^2 K_2 t)}{(q_e K_2 t + 1)} \quad (7)$$

Where K_1 and K_2 are the pseudo-first-order and pseudo-second-order constant.

Biosorbents Characterizations

The Fourier Transform Infrared Spectroscopy (Nicolet 50) in the 4000 cm^{-1} - 400 cm^{-1} range was used to determine the biosorbent's functionality using the conventional KBr method. In this method, the pellet was prepared by mixing about 250 mg of KBr with approximately 1 mg of powder of *Azadirachta indica* Fruits in an agate mortar. Then the mixture was pressed at about 15 Pa for 2 min. A Quantachrome IQ-XR-XR (Stat.) instrument was used for BET analysis of the N_2 adsorption and desorption of the biosorbent, which was degassed for 24 hours at 130°C. The surface area was calculated using the BET equation, the total pore volume was calculated using the BJH model, and the average pore size was calculated using the DFT model. The surface morphology of the biosorbent was examined using Field Emission Scanning Electron Microscopy (JSM-761FPlus), employing a Quanta 200F microscope set to an accelerating voltage of 20 kV for the analysis. To facilitate the creation of a conductive layer on the surface, the biosorbent sample was coated with gold (Au) under an argon pressure of 10-2 mbar for 60 seconds. Energy-dispersive X-ray spectroscopy was utilized to examine the elements found in the biosorbent before and after the biosorption.

RESULTS AND DISCUSSION

Functional Groups Analysis

The FTIR spectra of biosorbent before and after the adsorption of heavy metal ions have been shown in Fig.-2. There were several peaks corresponding to the different functional groups and bonding contained in the biosorbent. The peaks appearing at 3430.10 cm^{-1} corresponded to the OH (hydroxyl), -NH (amine) bond vibration which indicated that the neem fruit biosorbent has lignocellulosic structures, protein, and pectic compound. The band at ~ 2950-2900 cm^{-1} and ~2850-2800 cm^{-1} was due to symmetrical and asymmetrical – CH_2 and -C-H stretching vibration in the methylene and methyl groups, respectively which suggested the presence of lipid content.[15] The peaks at 1745.65 $cm^{-1}$and 1650-1655 cm^{-1} observed in spectra due to -C=O (carboxy) stretching indicate the presence of amides, ketones, aldehydes, esters, and carboxylic acids

functional groups. The peaks observed at 1400-1420.62 cm-1 and 1234.52 cm^{-1} are associated with the highly asymmetric -COO and -CH_3 groups, which are indicative of protein presence. The peaks at 1000-1350 cm^{-1} have been assigned due to the -C-O-C stretching in the groups in the glycosidic ether vibrations present in cellulosic groups.[16] The adsorption of heavy metal ions at around 418.46 cm^{-1} due to the metal bonding with the functional groups on the biosorbents has been shown in Fig.-2. It was noted from the spectra that there was no significant alteration in the band shift after the adsorption of metal ions, indicating that complex formation with these metal ions is unlikely to occur. Consequently, ionic exchange may occur between the functional groups on the surface of the neem biosorbent and the metal ions.

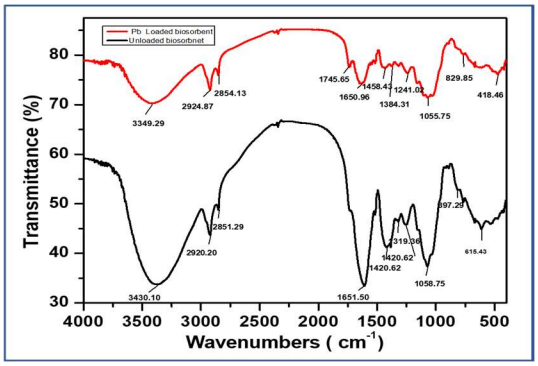


Fig.-2: FTIR Spectra of Biosorbent-Raw, and Pb Loaded Biosorbent

BET Analysis

The BET equation was utilized to calculate the surface area, while the BJH model was applied to assess the total pore volume and pore size. Additionally, the DFT model was used to ascertain the average pore size. The nitrogen adsorption-desorption isotherm and the pore size distribution for the biosorbents are illustrated in Fig.-3. The findings indicated that the BET surface area measured 5.533 m^2/g, the pore volume was 0.296 cm^3/g, and the pore diameter was determined to be 1.057 Å. According to the IUPAC classification, the N_2 adsorption and desorption isotherm of the biosorbent demonstrates a type IV isotherm along with H3 hysteresis. Awe *et al*. showed similar results in their research study.[17]

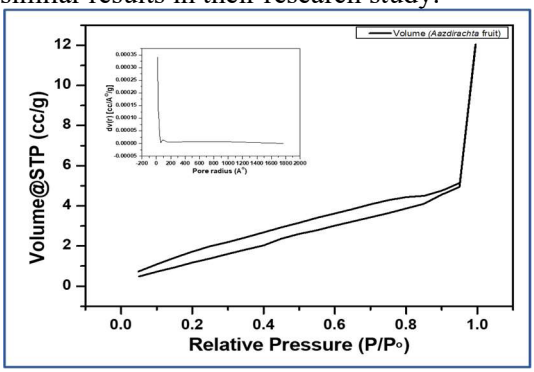


Fig.-3: N_2 Adsorption-desorption Isotherm and Distribution of Pore Sizes for Biosorbent

FESEM Analysis

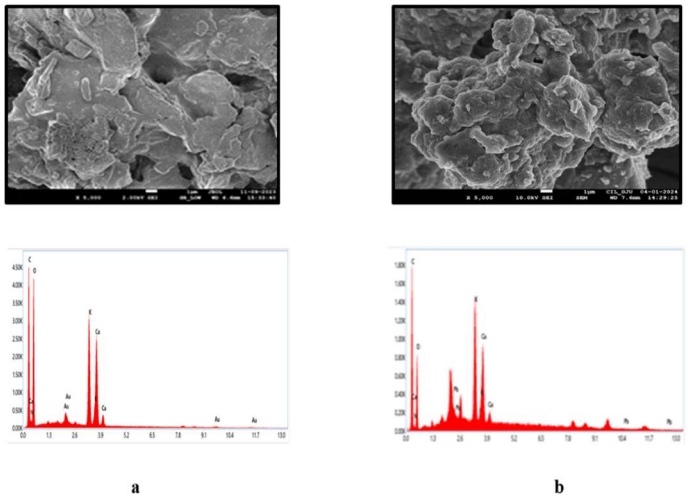
FESEM micrographs of metal-loaded and unloaded biosorbents of *Azadirachta indica* Fruits *are* shown in Fig.-4. Before the adsorption of the metal ions on the biosorbents, the surface of the biosorbents seems irregular and heterogeneous. it was found that unloaded biosorbents of neem (*Azadirachta indica*) have rough and rigid surfaces with a number of porous cavities. After the adsorption of metal ions, no longer cavities and porous were observed on the surface of the biosorbents and all cavities were occupied with metal ions and it had to destroy its heterogeneity, more homogenous surface appearance.[18]

Batch Studies

Effect of *p*H

The *p*H level of the metal ions solution plays a crucial role in influencing both the binding sites available on the biosorbent surface as well as adsorbate. The effect of *p*H (2-9) on the biosorption efficiency of Pb

(II) was studied at a constant time of 60 minute and metal ions concentration of 20 mg/L and 2g/L of biosorbent dosage.[19] The results are shown in Fig.-5.



a b

Fig.-4: FESEM and EDS Micrographs of Unloaded and Loaded Lead Metal Ions Neem Fruit Biosorbent

It was shown that the removal efficiency increased from *p*H 2 to 5 and then decreased. At the lower *p*H, active sites are not available for the Pb (II) metal ions adsorption because, at the lower *p*H, functional groups (-NH_2 and -OH) of the biosorbent get protonated in the form -NH_3^+ and -OH_2^+ groups. So, at lower *p*H, there will be repulsion between the positively charged heavy metals and protonated functional groups. As we increase the *p*H, more functional would be exposed, and active sites release their proton into the solution to carry a negative charge to enhance the binding capacity of the metal ions. An increased pH of the solution, would produce a more negative charge in the solution which is more appropriate for the heavy metal ions uptake. At higher pH levels, removal efficiency decreased due to the production of Pb $(OH)_2$ metal ions hydroxide. The results agree with previous studies.[20]

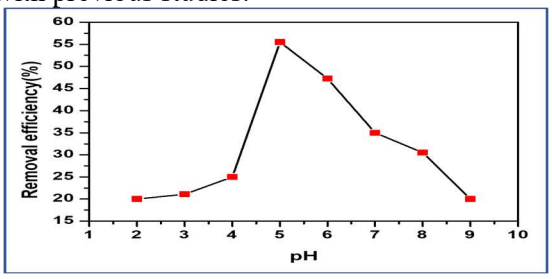


Fig.- 5: Effect of pH on Removal Efficiency for Pb (II) on Neem Fruits Biosorbent

Effect of Biosorbent Dose

The effect of biosorbent dosage (2-10 g/L) was evaluated for the removal of Pb (II) at optimum *p*H 5 and at a concentration of 20 mg/L in 20 ml of metal ions solution at 60 minutes. It was observed that the biosorption efficiency increased with the dosage of Neem fruit biosorbent, with the maximum removal achieved at 2 g/L (0.04/20 mL). However, increasing the amount of biosorbent beyond 2g/L did not significantly affect the adsorption rate as shown in Fig.-6. The adsorption efficiency increases with an increase in adsorbent dose, because more available of active sites for heavy metal ions, further increased the biosorbents dose, percentage removal was constant due to the increase in the dose, there are partial aggregation of biomass, resulting in a decrease in the number of active sites on the surface of biomass.[21] So, increasing the biomass concentration over the optimum dose does not lead to appreciate improvement in removal efficiency.

Effect of Concentration

We investigated the impact of different initial metal ion concentrations, ranging from 20 to 80 mg/L, on the biosorption efficiency of neem fruits, utilizing an optimized biosorbent dosage of 2 g/L and a *p*H level of 5. Based on the experimental data, the results indicated that as the initial concentration of Pb (II) metal ions

in the solution increased, the removal efficiency of neem fruit biosorbents decreased gradually as shown in Fig.-7.

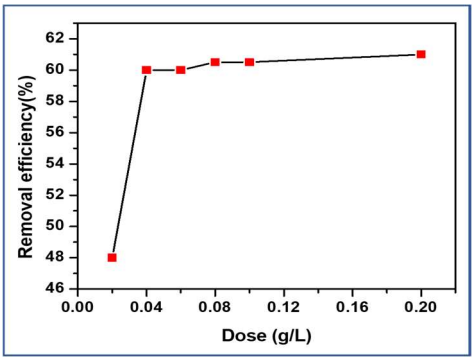


Fig.-6: Effect of Dose on Removal Efficiency for Pb (II) on Neem Fruits Biosorbent

It was found that removal efficiency was 60 % at the 20 mg/L concentration of the initial metal ions solution and decreased at higher concentrations. A greater concentration gradient between the solution and the biosorbent surface resulted from an increase in the concentration of metal in the solution. The movement of metal ions between the solid and aqueous phases is facilitated by this concentration gradient. Consequently, until the biosorbent is saturated, the metal adsorption is increased. On the other hand, as the initial concentration of metal ions increased, the amount of metal removed from the solution decreased. There are sufficient active binding sites for the metal ions in solution on the biosorbent surface at low metal concentrations. These patterns are possibly from the concept that at the lower concentration, many active sites are present on the biosorbent and these sites become more occupied at higher concentration.[22]

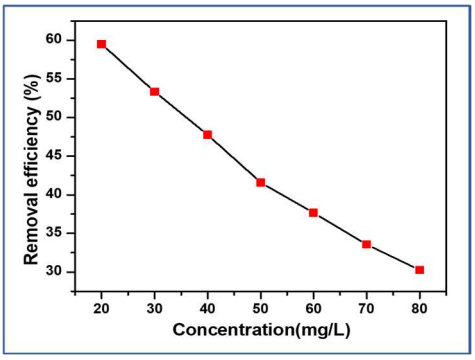


Fig.-7: Effect of Concentration on Removal Efficiency for Pb (II) on Neem Fruits Biosorbent

Effect of Contact Time

The removal efficiency of Pb metal ions at different contact times (30, 60, 90, 120, 150, 180, and 210 min) was also analyzed (Fig.-8). A gradual increase in removal efficiency was observed as the time was increased from 30 min to 90 min at 30°C, and it attained equilibrium in 90 min.[23] Upon extending the contact time further, there was no noticeable change in the percentage removal efficiency as shown in Fig.-8. It was observed that initially, the rate of biosorption is higher because of readily available active sites on the biosorbent surface, but as the adsorption proceeds, these sites get occupied resulting in lower rates of adsorption. After equilibrium, saturation is reached; all pores are filled, resulting in reduced metal ion uptake. So, it was concluded that the adsorption of heavy metal ions on the biosorbents is governed by the external mass transfer.[24] Removal efficiency of biosorbent for Pb metal ions was found 70 % respectively.

Adsorption Experiments Modelling

To acquire further details regarding the biosorption mechanism of lead metal ions by biosorbent the adsorption isotherms were used to evaluate the equilibrium data. Studies on adsorption isotherms were conducted using two primary models, the Langmuir and Freundlich adsorption isotherm models. The adsorption parameters (K_L, K_f, 1/n, and q_{max}) and regression coefficient (R^2) were obtained for both models. The Langmuir parameter, q_{max} reflects the adsorption capacity of the material i.e. saturation of monolayer

on the surface of biosorbents at the equilibrium, and the Langmuir constant, K_L depicts the stronger affinity of the metal ions with the biosorbent surface.

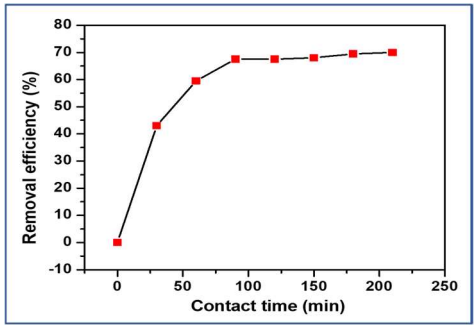


Fig.-8: Effect of Contact Time on Removal Efficiency for Pb (II) on Neem Fruits Biosorbent

The Freundlich isotherm parameters 1/n and K_f, expressed as the heterogeneity factor, indicate the adsorption intensity and are related to the adsorption capacity of the material, respectively. The data fit well with the Langmuir model, with regression coefficients (R^2) of 0.99 for Pb (II) as shown in Table-1. The Langmuir equation fitting to experimental data suggests a homogeneous biosorbent surface. The metal ions get adsorbed on surface sites with similar binding energy levels. According to the Langmuir equation fitted to the experimental data, the biosorbent surfaces are homogeneous. Adsorbed heavy metal ions have surface sites with comparable binding energy levels. The maximum monolayer adsorption capacities (q_{max}) for Pb (II) were found to be 14.71 mg/g. The findings indicate that biosorption adheres to the Langmuir nonlinear isotherm, demonstrating monolayer adsorption on the biosorbent surfaces, which possess a limited number of active sites.[25]

Table-1: Linear and Non-Linear Parameters for Langmuir and Freundlich Isotherms for the biosorption of the Pb (II)

Isotherm models	Parameter	Pb (II)
Freundlich (non-linear)	1/n	0.33
	K_f (mg/g) $(L/mg)^{1/n}$	3.38
	R^2	0.95
Freundlich (linear)	1/n	0.36
	K_f (mg/g) $(L/mg)^{1/n}$	2.98
	R^2	0.95
Langmuir (non-linear)	(q_{max}) (mg/g)	14.6
	K_L(L/mg)	0.085
	R^2	0.99
Langmuir (linear)	q_{max} (mg/g)	14.71
	K_L(L/mg)	0.085
	R^2	0.99

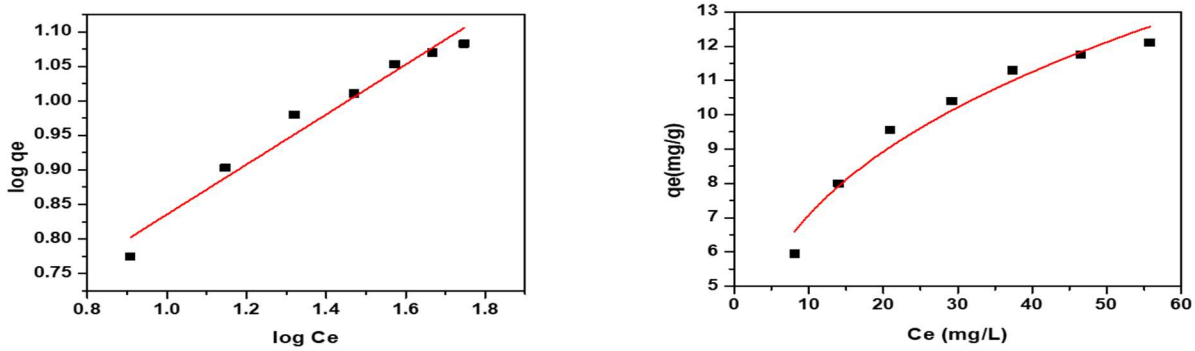


Fig.-9: Freundlich Linear and Nonlinear Isotherm on Neem (*Azadirachta indica*) Fruit Biosorbent for Pb (II) Metal Ion

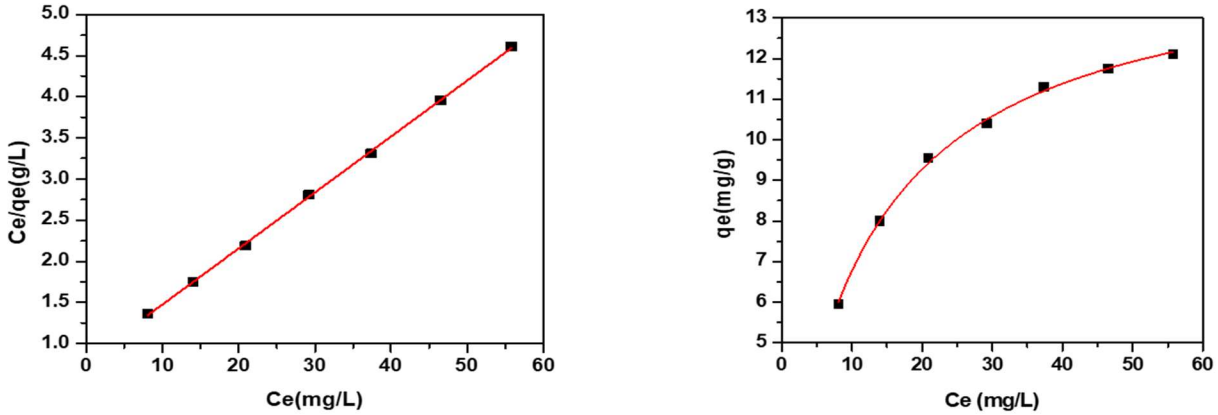


Fig.-10: Langmuir Linear and Nonlinear Isotherm on Neem (*Azadirachta Indica*) Fruit Biosorbent For Pb (II) Metal Ion

Kinetics Study

From the results of pseudo-second-order kinetics, the rate constant (K_2) and adsorption capacity (Q_e) were also increased with the rising temperature from 303K to 323K as shown in Table-2. This is due to the fact that when the temperature rises, the kinetic energy of the molecules precipitating in the reaction rises as well. This increases the number of collisions of the heavy metal ions and the surface of the biosorbents. The results reported here show that the adsorption process is chemically initiated by temperature. The calculating adsorption capacities for Pb (II) metal ions were close to the experimental values of adsorption capacities in the pseudo second order model suggesting that the adsorption process was going with pseudo second order. The fitting of the kinetic models to the data from the experiments was compared using the regression coefficient (R^2). It was found that the regression coefficient (R^2) was very high and close to 1 for Pb (II) metal ions in the pseudo-second-order model (Fig 12).[26] It is concluded that the pseudo-second-order kinetics model was best fitted for experimental data for Pb (II) which shows that the adsorption of metal ions on the biosorbents was dependent on the adsorption capacities not on the concentration of the reactants. [27] The fitting of experimental data to the pseudo-first and pseudo-second-order kinetic models suggested that the data was best fitted with pseudo-second-order kinetics for Pb (II) metal ions. Pb (II) demonstrated evidence of chemisorption or effective interaction between metal ions and biosorbent.[28]

Table-2: Kinetics Parameters of Pb (II) Metal Ions on Neem Fruits Biosorbent

Kinetics models	Parameter	303K	313K	323K
PFO (non-linear)	$Q_{e,\,cal}$(mg/g)	6.57	6.76	6.76
	K_1(min^{-1})	0.04	0.039	0.036
	R^2	0.9631	0.9634	0.9439
PFO (linear)	$Q_{e,\,cal}$(mg/g)	2.098	3.053	2.6239
	K_1(min^{-1})	0.01	0.017	0.01
	R^2	0.87	0.95	0.95
PSO (non-linear)	$Q_{e,\,cal}$ (mg/g)	7.25	7.48	7.55
	K_2 (g/mg min^{-1})	0.0083	0.0085	0.0086
	R^2	0.9856	0.9978	0.9998
PSO (linear)	Q_{ecal}(mg/g)	7.11	7.41	7.51
	K_2 (g/mg min^{-1})	0.0085	0.0091	0.0092
	R^2	0.9966	0.9934	0.9910
	Q_e (exp.) (mg/g)	7.5	7.5	8

PFO* =Pseudo First Order; PSO*= Pseudo Second Order

Thermodynamic Studies

The free energy change (ΔG^o), entropy change (ΔS^o), and enthalpy change (ΔH^o) were calculated to investigate the effect of temperature on the adsorption of heavy metal ions on the biosorbents. The equilibrium constant (K_C) is calculated by following the equation (8).[29]

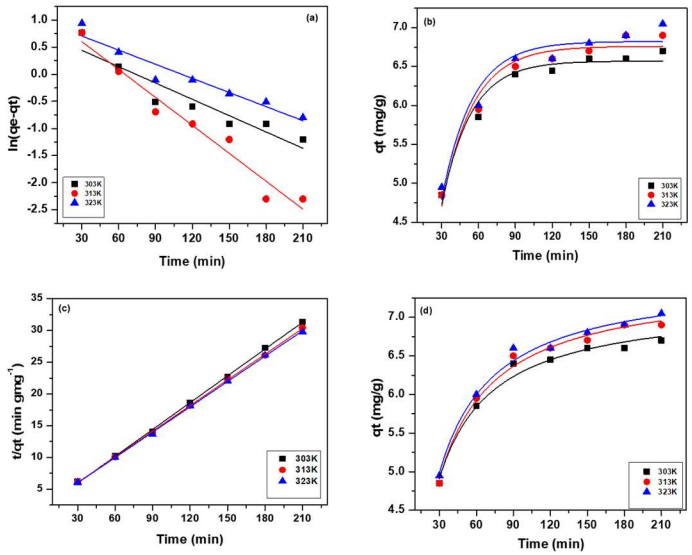


Fig.-12: Pseudo-First-Order (a) Linear (b) Nonlinear and Pseudo Second Order (c) Linear (d) Nonlinear on Neem (*Azadirachta indica*) Fruit Biosorbent for Pb (II) Metal Ion

$$K_c = \frac{Q_e}{C_e} \quad (8)$$

The entropy change (ΔS^o) and entropy change (ΔH^o) values calculated by Van't Hoff equation

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (9)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (10)$$

Where,

ΔG^o= Gibbs free energy change, ΔS^o= Entropy change, ΔH^o= Enthalpy change, K_c = Equilibrium constant, and T= temperature.

Table-3: Thermodynamics Parameters of Pb (II) on Neem Fruits Biosorbent

Temp (K)	1/T	K_C	ln K_C	ΔG^0 (KJ/mol)	R^2	ΔH^0 (KJ/mol)	ΔS^0 (J/K/mol)
303K	0.0033003	1.78	0.575	-0.16	0.99	3.569	16.56
313K	0.0031948	1.86	0.619	-1.61			
323K	0.0030956	1.94	0.663	-1.78			

In the adsorption of heavy metal ions Pb (II) on the biosorbents, the values of Gibbs free energy (ΔG^o) at the 303K, 313K, and 323K temperatures were negative which suggests that the adsorption process of metal ions were spontaneous and the there exists a proportional relationship between temperature.[30] The Gibbs free energy (ΔG^o) which is the negative value of ΔG^o rises with an increase in temperature i.e. decreases with the temperature, demonstrating that higher temperature promotes the heavy metal adsorption process. The positive value of enthalpy change (ΔH^o) for the adsorption of heavy metal ions Pb (II) depicts that the adsorption process was endothermic. Also, the positive entropy change (ΔS^o) values confirmed that the mechanism of biosorption is irreversible and stable.[31] The characterization results and experimental data allow for the conclusion that the adsorption of metal ions Pb (II), from the aqueous solution was achieved through an ion exchange method. This is evidenced by the absence of significant changes in the band shift after the adsorption of the metal ions, indicating that the formation of complexes with the metal ions is unlikely. The Neem (*Azadirachta indica*) fruit biosorbent exhibited the ability to remove 70% of Pb (II) from the aqueous solution with 20 mg/L of lead at a biosorbent dose of 2g/L. the study observed that removal efficiency increased as contact time increased, reaching saturation in approximately 90 minutes at *p*H~5. The thermodynamic analysis indicated that the adsorption of these heavy metal ions was a spontaneous and endothermic process.[32]

CONCLUSION

The work present in this study outlines the effectiveness of neem (*Azadirachta indica*) fruit as a potential biosorbent for the removal of Pb (II) from wastewater. The neem fruit biosorbent exhibited the ability to

remove 70% of Pb (II) from the aqueous solution with 20 mg/L of lead at a biosorbent dose of 2g/L. the study observed that removal efficiency increased as contact time increased, reaching saturation in approximately 90 minutes. The Langmuir and Freundlich isotherms equations were used to characterize the equilibrium data. Analysis of the isotherm equations and regression coefficient R^2 indicates that the Langmuir non-linear isotherm provided a better fit to the experimental data compared to the Freundlich model. The analysis of the kinetics study revealed that biosorption of lead was better fitted with the Pseudo second-order kinetic model. The thermodynamic analysis indicated that the adsorption of these heavy metal ions was a spontaneous and endothermic process. The research indicates that neem (*Azadirachta indica*) fruit has the potential to be extensively studied as a highly effective biosorbent for removing metal ions from water solutions and since its economic value as a waste product, low cost, and environment friendly.

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CONFLICT OF INTERESTS

The author declares that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

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